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(56) Documents cited J. Org. Chem 1972, *37*, 1712—1717 - See Ref. to 4,9-Dihydro(2,3-B) Thiophene-4,9 Dione
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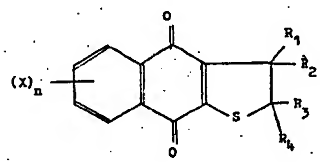
(54) 4,9-Dihydronaphtho[2,3-b]thiophene-4,9-diones

(57) 4,9-Dihydronaphtho[2,3-b]thiophene-4,9-diones of the formula



(I)

wherein

R_1 is hydrogen or optionally substituted alkyl or aryl,

R_4 is hydrogen or optionally substituted alkyl, provided that R_1 and R_4 are not both hydrogen,

R_2 is hydroxyl when R_3 is hydrogen, or R_2 or R_3 together form a direct link,

X is hydrogen, halogen, hydroxyl, nitro, amino, alkylamino, arylamino, acylamino, sulphonate, alkoxy, mercapto, alkylmercapto or arylmercapto and n is zero or an integer from 1 to 4, are prepared by reacting a 1,4-naphthoquinone with a compound of the formula $HSCH(R^4)COR$, or with a precursor thereof, in the presence of a basic catalyst. These compounds are used for the colouration of synthetic textile materials.

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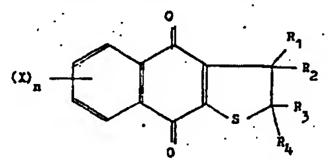
SPECIFICATION
Chemical Process

This invention relates to a chemical process and more particularly to a process for the preparation of certain 4,9-dihydronaphtho[2,3-b]thiophene-4,9-diones, also known as thiophanthraquinones.

According to the present invention there is provided a process for the preparation of thiophenthraquinones having the formula:


(I)

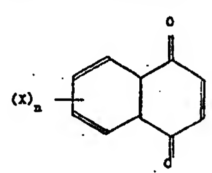
wherein R_1 represents a hydrogen atom or an optionally substituted alkyl or aryl group;

R_4 represents a hydrogen atom or an optionally substituted alkyl group, provided that R_1 and R_4 are not both hydrogen atoms;

R_2 represents a hydroxyl group when R_3 is hydrogen, or R_2 and R_3 together form a direct link;

X represents a hydrogen atom, a halogen atom or a hydroxyl, nitro, amino, alkylamino, arylamino, acylamino, sulphonic acid, alkoxy, mercapto, alkylmercapto or arylmercapto group, and *n* is zero or an integer from 1 to 4,

which comprises reacting a 1,4-naphthoquinone of the formula:


(II)

wherein X and *n* have the meanings defined above, with a thiol of the formula:

$$\begin{array}{c} R^4 \\ | \\ HS—CH—COR_1 \end{array} \qquad (III)$$

wherein R_1 and R_4 have the meanings defined above, or with a precursor thereof, in the presence of a basic catalyst.

The alkyl groups represented by R_1 and R_4, and in the alkylamino and alkylmercapto groups represented by X are preferably lower alkyl groups. The substituted alkyl groups represented by R_1 and R_4 are preferably substituted lower alkyl groups. The alkoxy groups represented by X are preferably lower alkoxy groups. The optionally substituted aryl groups represented by R^1 are preferably optionally substituted phenyl groups. The acylamino groups represented by X are preferably of the formula —NHCO . T or —$NHSO_2T$ wherein T is a lower alkyl group of an optionally substituted phenyl group.

By the terms "lower alkyl" and "lower alkoxy" we mean alkyl and alkoxy groups respectively which contain from 1 to 4 carbon atoms.

Examples of the alkyl groups represented by R_1 and R_4 are methyl, ethyl, *n*-propyl isopropyl and *n*-butyl, and examples of substituted alkyl groups represented by R_1 and R_4 are hydroxyalkyl groups such as β-hydroxyethyl, alkoxyalkyl groups such as β-methoxyethyl, halogenoalkyl groups such as β-chloroethyl and β-bromoethyl, and cyanoalkyl groups such as β-cyanoethyl.

Examples of substituted aryl groups represented by R_1 are alkylaryl groups such as tolyl, alkoxyaryl groups such as methoxyphenyl, nitroaryl groups such as nitrophenyl, halogenoaryl groups such as chlorophenyl and bromophenyl and cyanoaryl groups such as cyanophenyl.

Examples of alkylamino groups represented by X are methylamino and ethylamino.

Examples of arylamino groups represented by X are phenylamino and tolylamino.

Examples of alkylmercapto groups represented by X are methylmercapto and ethylmercapto.

Examples of arylmercapto groups represented by X are phenylmercapto and tolylmercapto.

Examples of alkoxy groups represented by X are methoxy and ethoxy.

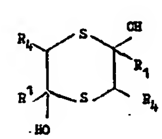
Examples of acylamino groups represented by X are acetylamino, benzoylamino, methylsulphonylamino, ethylsulphonylamino and phenylsulphonylamino.

Examples of halogen atoms represented by X are chlorine and bromine atoms.

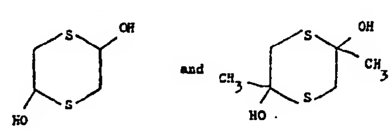
The reaction is preferably carried out in an inert organic solvent and at an elevated temperature. Examples of suitable inert organic solvents are methanol, ethanol, dioxan and methoxyethanol. The reaction temperature may be from 20 to 180°C, and is conveniently the reflux temperature of the solvent-containing reaction mixture.

Examples of the compounds of formula (II) which may be used in the process are 1,4-naphthoquinone, 5-amino-1,4-naphthoquinone, 5-acetylamino-1, 4-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone.

Precursors of the compounds of formula (III) which may be used are thioaldehyde dimers of the formula:


(IV)

wherein R_1 and R_4 have the meanings defined above. Examples of such thioaldehyde dimers of formula (IV) which may be used are:



Alternatively, the thiol of formula (III) may be replaced by a mixture of approximately equimolecular quantities of a compound of the formula:

$$Y\text{—}\underset{}{\overset{R_4}{\overset{|}{C}H}}\text{—}COR_1 \quad \text{(IV)}$$

wherein R_1 and R_4 have the meanings defined above and Y is a halogen atom, and an alkali metal hydrogen sulphide.

Examples of the halogen atoms represented by Y are chlorine and bromine atoms.

Examples of the alkali metal hydrogen sulphides which may be used together with the compound of formula (V) are sodium hydrogen sulphide and potassium hydrogen sulphide.

Examples of the compounds of formula (V) which may be used are chloroacetaldehyde, chloroacetone, chloromethyl methoxymethyl ketone, α-chloropropionaldehyde, α-chloroethyl methyl ketone, ethyl chloroacetylacetate, chloroacetylacetamide and chloroacetylacetanilide.

Examples of basic catalysts which may be used are triethylamine, piperidine, morpholine, pyridine and tetraethylammonium hydroxide. The amount of basic catalyst required will in general be from 0.05 to 1.0 mol per mol of the compound of formula (II), although amounts outside this range may be used if necessary. Pyridine may be used as the solvent in addition to its function as a base.

The formation of compounds of formula (I) in which R_2 and R_3 together form a direct link proceeds *via* the compounds in which R_2 is hydroxyl and R_3 is hydrogen, but if preparation of the former compounds is desired it is not necessary to isolate the latter. If a compound of formula (I) in which R_2 is hydroxyl and R_3 is hydrogen is isolated, it may be converted into the compound of formula (I) in which R_2 and R_3 together form a direct link by heating the former compound in an organic solvent, optionally in the presence of a basic catalyst, which may be the same basic catalyst as that used in the initial stage of the process.

The compounds of formula (I) may be isolated from the reaction mixture by conventional means, for example, by cooling the reaction mixture, filtering off the product which separates washing it with fresh solvent and drying. The product may be purified by recrystallisation if desired.

Certain of the products of formula (I) obtained according to the process of the invention are novel compounds, and as such constitute a further feature of the invention.

The thiophanthraquinones obtained according to the present process find utility as dyestuffs when sufficiently strongly coloured and/or as intermediates in the preparation of dyestuffs.

The compounds which are capable of being used as dyestuffs and which are free from sulphonic acid groups, when applied in the form of an aqueous dispersion to synthetic textile materials, give red shades having good fastness to the test which are conventionally applied to such coloured textile materials.

Dyestuffs obtained according to the invention which are free from sulphonic acid groups may also be applied to synthetic textile materials by the method of sublimation transfer printing, in which the dyestuff is made up into a printing ink which is used to print a design on to a transfer material, usually paper. The printed transfer material is dried, placed with the printed surface in contact with the synthetic textile material which is to be printed, and the composite is then subjected to slight pressure and to a temperature from about 190° to about 210°C for a time of from about 15 to 90 seconds, whereby the design is transferred from the transfer material on to the synthetic textile material. The prints so obtained have similar fastness properties to the dyeings obtained using the dyestuff in the form of an aqueous dispersion.

These methods of application and the coloured synthetic textile materials so obtained constitute further features of the invention.

Examples of the synthetic textile materials to which the dyestuffs obtained according to the process of the present invention may be applied are cellulose triacetate, polyamide and especially aromatic polyester textile materials.

The invention is illustrated but not limited by the following Examples in which parts and percentages are by weight.

Example 1

9.25 parts of chloroacetone are added during $1\frac{1}{2}$ hours to a mixture of 22.4 parts of a 25% aqueous solution of sodium hydrogen sulphide and 20 parts of methanol at 0—5°C. The solution is stirred at 0—5°C for a further 2 hours and then allowed to warm to 20°C, when 15.8 parts of 1,4-naphthoquinone, 70 parts of methanol and 2 parts of triethylamine are added. After an initial exothermic reaction which raised the temperature of the reaction mixture to about 40°C, the mixture is stirred at 20°C for 1 hour and then under reflux for 2 hours. The reaction mixture is cooled and the product is filtered off, washed with methanol and recrystallised by extraction into ethanol. The 3-methyl-4,9-dihydronaphtho[2,3-b]thiophene-4,9-dione so obtained melts at 178—179°C.

Example 2

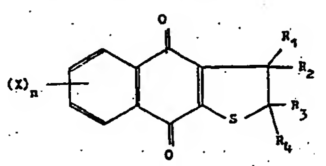
5.48 parts of 2-bromopropionaldehyde are added during 30 minutes to a mixture of 8.96 parts of a 25% aqueous solution of sodium hydrogen sulphide and 50 parts of methanol at 0—5°C. The solution is stirred at 0—5°C for a further 1 hour, after which 3.14 parts of naphthoquinone and 2.0 parts of triethylamine are added. The mixture is then allowed to warm up to 20°C, when a yellow solution of 2-methyl-3-hydroxy-4,9-dihydronaphtho[2,3-b]2,3-dihydrothiophene-4,9-dione is obtained which may be precipitated by dilution with water and isolated by filtration.

A solution of this intermediate in 50 parts of ethanol, or alternatively the reaction mixture containing the intermediate, is stirred and heated under reflux for 2 hours during which time the

product comes out of solution. After cooling the reaction mixture the product is filtered off, washed with methanol and dried, when 2-methyl-4,9-dihydronaphtho[2,3-b]thiophene-4,9-dione is obtained as yellow-brown crystals. Recrystallisation from acetic acid gives needle crystals which melt at 242—243°C.

Claims

1. A process for the preparation of thiophanthraquinones having the formula:



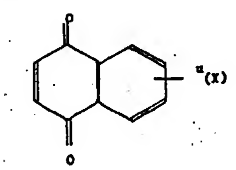
(I)

wherein R_1 represents a hydrogen atom or an optionally substituted alkyl or aryl group;

R_4 represents a hydrogoen atom or an optionally substituted alkyl group, provided that R_1 and R_4 are not both hydrogen atoms;

R_2 represents a hydroxyl group when R_3 is hydrogen, or R_2 and R_3 together form a direct link;

X represents a hydrogen atom, a halogen atom or a hydroxyl, nitro, amino, alkylamino, arylamino, acylamino, sulphonic acid, alkoxy, mercapto, alkylmercapto or arylmercapto group, and *n* is zero or an integer from 1 to 4, which comprises reacting a 1,4-naphthoquinone of the formula:



(II)

wherein X and *n* have the meanings defined above, with a thiol of the formula:

$$\mathrm{HS{-}\underset{\displaystyle R^4}{\overset{}{CH}}{-}COR_1} \quad \text{(III)}$$

wherein R_1 and R_4 have the meanings defined above, or with a precursor thereof, in the presence of a basic catalyst.

2. A process as claimed in claim 1 wherein the reaction is carried out in an inert organic solvent.

3. A process as claimed in claim 1 or claim 2 wherein the reaction is carried out at an elevated temperature.

4. A process as claimed in claim 3 wherein the reaction temperature is the reflux temperature of the solvent-containing reaction mixture.

5. A process as claimed in any one of claims 1 to 4 wherein in place of the thiol there are used approximately equimolecular quantities of a compound of formula:

$$\mathrm{Y{-}\underset{\displaystyle R_4}{CH}{-}COR_1}$$

wherein R_1 and R_4 have the meanings defined in claim 1 and Y is a halogen atom, and an alkali metal sulphide.

6. A process for the preparation of thiophanthraquinones having the formula defined in claim 1 wherein R_2 and R_3 together form a direct link, which comprises heating in an organic solvent a thiophanthraquinone having the formula defined in claim 1 wherein R_2 is hydroxyl and R_3 is hydrogen.

7. A process as claimed in claim 6 wherein the reaction is carried out in the presence of a basic catalyst.

8. A process as claimed in any one of claims 1 to 7 wherein there are used a thiol and a naphthoquinone respectively having the formulae defined in claim 1, in which the alkyl groups represented by R_1 and R_4 in the thiol and in the alkylamino and alkylmercapto groups represented by X in the naphthoquinone, are lower alkyl groups.

9. A process as claimed in any one of claims 1 to 8 wherein there is used a thiol having the formula defined in claim 1 in which the substituted alkyl groups represented by R_1 and R_4 are substituted lower alkyl groups.

10. A process as claimed in any one of claims 1 to 9 wherein there is used a naphthoquinone having the formula defined in claim 1 in which the alkoxy groups represented by X are lower alkoxy groups.

11. A process as claimed in any one of claims 1 to 10 wherein there is used a thiol having the formula defined in claim 1 in which the optionally substituted aryl group represented by R_1 is an optionally substituted phenyl group.

12. A process as claimed in any one of claims 1 to 11 wherein there is used a naphthoquinone having the formula defined in claim 1 in which the acylamino groups represented by X have the formula —NHCO.T or —$NHSO_2$.T in which T is a lower alkyl group or an optionally substituted phenyl group.

13. A process as claimed in claim 5 substantially as hereinbefore described in the foregoing Example 1 or Example 2.

14. Thiophanthraquinones whenever obtained by a process as claimed in any one of the preceding claims.

15. A process for the colouration of synthetic textile materials which comprises applying to the synthetic textile material an aqueous dispersion of a thiophanthraquinone as claimed in claim 14.

16. A process for the colouration of synthetic textile materials by transfer printing, which comprises making up into a printing ink a thiophanthrquinone as claimed in claim 14, printing a design on to a transfer material using the said printing ink, drying the printed transfer material, placing the printed surface of the printed transfer material in contact with the synthetic textile material which is to be printed and then subjecting the composite to slight pressure and to a temperature from approximately 190° to approximately 210°C for a time from 15 to 90 seconds, whereby the design is transferred from

the transfer material to the synthetic textile material.

17. A process as claimed in claim 15 or claim 16 wherein the synthetic textile material is an aromatic polyester textile material.

18. Synthetic textile materials whenever coloured by a process as claimed in any one of claims 15 to 17.

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